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THE ACTIVITY QUOTIENT AS A FUNCTION OF TIME FOR SOME CHEMICAL REACTIONS

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ABSTRACT

The logarithm of the activity quotient was found to be proportional to the logarithm of the elapsed time for many types of homogeneous chemical reactions that occur in isothermal closed systems. The reactions investigated include gas-phase and liquid-phase reactions in both aqueous and nonaqueous solvents. The kinetic data used in this evaluation were solicited from investigators whose results had been reported in the literature.

INTRODUCTION

An investigation was undertaken to determine whether thermodynamic quantities associated with a chemical reaction in an isothermal closed system change in a describable manner as the reaction proceeds. Because no theoretical study concerning the time dependence of thermodynamic quantities associated with a chemical reaction in an isothermal closed system was found in the literature, this investigation has been strictly empirical, and is essentially a study of the time dependence of the activity quotient for a variety of reactions.

NATURE OF THE APPROACH

Consider an isothermal closed system in which the following chemical reaction occurs:

$$aA + bB + \ldots + mM \rightarrow cC + dD + \ldots + nN \,. \tag{1}$$

The activity quotient Q is the only variable of the system and is defined by the following convention:

$$Q = \frac{[C]^c[D]^d \ldots [N]^n}{[A]^a[B]^b \ldots [M]^m} \,. \tag{2}$$

The quantities in brackets are the activities of the products and the reactants, and the exponents are the stoichiometric coefficients of reaction (1).

The free-energy difference ΔG between the products and the reactants of reaction (1) is related to the activity quotient by the following expression:

$$\Delta G = \Delta G^o + RT \ln(Q) \,, \tag{3}$$

where ΔG^o is the free-energy difference when all the products and reactants are in their standard states, R is the gas constant, and T is the absolute temperature. According to thermodynamics, the free-energy function ΔG must be negative for reaction (1) to proceed spontaneously in the direction indicated. If it is assumed that the reaction does proceed as illustrated, then the value of the activity quotient, as defined, will increase, and, from equation (3), the free-energy function will also increase. Partial differentiation of equation (3) with respect to time results in a relationship between the rate of increase of the free-energy function and that of the activity quotient:

$$\left[\frac{\partial\, \Delta G}{\partial t}\right]_T = RT \left[\frac{\partial \ln(Q)}{\partial t}\right]_T \,. \tag{4}$$

Thus, the study of the activity quotient Q as a function of time is equivalent to a study of the free-energy function ΔG as a function of time.

The actual kinetic data with which this study was carried out were solicited from investigators whose results had been reported in the literature and were restricted to processes that occurred in isothermal closed systems. The reactions were further restricted to those that took place at low pressures or in dilute solutions. Thus, the partial pressures or concentrations of reacting species approximated their activities, and the activity quotient at various time intervals could thereby be calculated from the kinetic data.

COMPUTED CORRELATION

The rate of change of the logarithm of the activity quotient appears to be inversely proportional to the elapsed time for a majority of the reactions investigated:

$$RT\left[\frac{\partial \ln(Q)}{\partial t}\right]_T \propto \frac{1}{t} . \qquad (5)$$

Relationship (5) indicates that the logarithm of the activity quotient is proportional to the logarithm of the elapsed time.

With the aid of an IBM 7094 data processing machine, the kinetic data were statistically analyzed to determine to what extent the logarithm of the activity quotient linearly correlated with the logarithm of the elapsed time. The three sigma reliability limits of the determination coefficient were computed for each reaction. For more than two-thirds of the 93 reactions investigated, the lower reliability limit exceeded 95 percent, which indicates a good correlation of the experimental data. Almost one-half of the reactions investigated have a lower reliability limit greater than 99 percent, which indicates an excellent correlation.

The 93 reactions investigated were distributed among those reported to be zero, first, second, third, and fractional orders, as is illustrated by table 1. More than two-thirds of the first- and second-order reactions showed a good correlation according to relationship (5). The number of reactions of the zero, third, and fractional orders was too small to determine the correlation according to relationship (5).

The reactions that showed a good correlation in table 1 were found to be those in which the overall reaction was homogeneous and could be represented by a single chemical equation, those in which all the products appeared and reactants disappeared according to the stoichiometry of the overall equation, those in which catalyzing effects, such as surface area or illumination, were not altered during the reaction, and those in which competitive reactions were absent.

GRAPHICAL CORRELATION

For the purpose of graphical evaluation of the empirical data, the terms of relationship (5) can be equated by the introduction of a constant of proportionality G_r:

$$RT\left[\frac{\partial \ln(Q)}{\partial t}\right]_T = \frac{G_r}{t} \; . \tag{6}$$

Integrating yields

$$\ln(Q) = \frac{G_r}{RT}\ln(t) + C \; , \tag{7}$$

where C is the constant of integration. If a quantity t_1 is defined as the time at which the activity quotient is unity, equation (7) may be expressed thus:

$$\ln(Q) = \frac{G_r}{RT} \ln \left(\frac{t}{t_1}\right). \tag{8}$$

The computed values of G_r and t_1 are listed in table 2 for a group of the reactions investigated.

Figures 1 to 11 illustrate graphically the high degree of correlation between the activity quotient and the elapsed time according to equation (7) for some of the reactions listed in table 2. Figures 1 to 4 illustrate gas-phase reactions, while figures 5 to 11 illustrate liquid-phase reactions. The first three liquid-phase reactions occur in aqueous solutions, the last four in nonaqueous ones.

Figures 1 and 2 illustrate the thermal decomposition of four organic compounds. The correlation between the activity quotient and the elapsed time is quite good for these reactions. The decomposition of acetaldehyde does show some deviation from linearity. Similar deviations from linearity were found with other organic decomposition reactions in which small amounts of hydrogen, carbon oxides, or simple hydrocarbons were found with the primary products. Since the partial pressures of the products and the reactant were determined from the overall pressure increase in the system, the presence of these secondary products would introduce errors.

The decomposition of hydrogen peroxide vapor, shown in figure 3, shows a high degree of correlation at the five temperatures of observation.

The correlation in figure 4 is not as good as that shown by the other gas-phase reactions, but it is comparable with the half-order kinetics used by the experimental investigator[5]. The reaction is heterogeneous. It was reported that the reaction might have been initially inhibited, which may explain the low value for the first data point.

Figure 5 illustrates an electron-transfer reaction in perchloric-acid solution. The correlation was quite good at the five temperatures at which this second-order reaction was observed. Other electron-transfer reactions in perchloric acid solutions also show good correlations.

Figure 6 illustrates an ionic reaction in aqueous solution at four temperatures. As in the case of the electron-transfer reactions, the correlation is quite good.

The reaction between ferricyanide and 2-mercaptoethanol in aqueous solution does not show as good a correlation as do the other reactions in aqueous solution, but the data points are somewhat erratic, as shown in figure 7.

The correlation between the activity quotient and the elapsed time is generally quite good for reactions in nonaqueous solutions. The reaction of cis-2-butene episulphide with triphenylphospine in three organic solvents shows a very high degree of correlation, as illustrated in figure 8. The reactions illustrated in figures 9 and 10 occur in dioxane and ethanol, respectively, and also show good correlations.

Figure 11 shows the reaction of styrene with iodine in carbon tetrachloride, and shows a considerable deviation from linearity. The investigator reported that the initial kinetics is three-halves order in styrene and first order in iodine[13].

CONCLUSION

This investigation shows that, for many types of homogeneous reactions in which the overall chemical reaction can be specified, the activity quotient varies with time in a describable manner. Because the free-energy function is closely related to the activity quotient, the time dependence of this function can be found for reactions whose kinetic behavior is adequately described by relationship (5). Eliminating $\ln(Q)$ between equation (3) and (8) yields

$$\Delta G = \Delta G^{\circ} + G_r \ln\left(\frac{t}{t_1}\right) . \qquad (9)$$

This equation would not be valid, of course, for positive values of ΔG.

A major limitation of a kinetic equation involving the activity quotient is the fact that it can only be applied to chemical reactions in which the nature of the overall reaction is known and in which all the products increase and reactants decrease in the stoichiometric proportions specified by the overall equation. Deviations from this requirement are common, being caused usually by the formation of secondary products.

Further investigation of the literature data is being made to determine more conclusively the applicability of the empirical approach presented in this paper.

ACKNOWLEDGMENTS

The author is indebted to Dr. H. M. Davis, former Professor of Chemical Metallurgy, Pennsylvania State University, for his valuable advice, to the computer staff at the NASA Lewis Research Center, and to Dr. E. R. Ryba, Assistant Professor of Metallurgy, Pennsylvania State University, for assistance in computer programming.

TABLE 1. - THE DISTRIBUTION OF THE NINETY-THREE REACTIONS INVESTIGATED AMONG THE VARIOUS ORDERS

Correlation	Order					Total
	0	1	2	3	Fractional	
Good (>95%)	1	26	31	8	0	66
Poor (<95%)	1	8	12	3	3	27

TABLE 2. - THE VALUE OF THE PARAMETERS G_r AND t_1 ASSOCIATED WITH VARIOUS CHEMICAL REACTIONS UNDER THE CONDITIONS CITED

Reaction investigated	Solvent or diluent	Initial concentration, molarity; or pressure, mm Hg	Reaction order	Temperature, °K	G_r, cal/mole	t_1, sec	Ref.
1. Decomposition of di-t-butyl peroxide $(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_2CO + C_2H_6$	None	173.5	1	428	2419	103	1
2. Decomposition of dimethyl ether $(CH_3)O \rightarrow CH_4 + H_2 + CO$	None	312	1	777	4427	1517	2
3. Decomposition of acetaldehyde $CH_3CHO \rightarrow CH_4 + CO$	None	363	2	791	2524	452	3
4. Decomposition of azo-isopropane $C_3H_7NNC_3H_7 \rightarrow N_2 + C_6H_{14}$	None	35.15	1	543	2246	1990	4
5. Decomposition of silver oxide $2Ag_2O \rightarrow 4Ag + O_2$	None	0	0.5	623	1873	47.61×10^4	5
6. Reduction of Pu(IV) by Fe(II) in perchloric acid solution Pu(IV) + Fe(II) → Pu(III) + Fe(III)	0.5M $HClO_4$	0.001148M + 0.001167M	2	293.4	1188	17.30	6
	0.5M $HClO_4$	0.001148M + 0.001166M	2	288.6	1178	29.77	6
	0.5M $HClO_4$	0.001148M + 0.001167M	2	283.4	1150	50.49	6
	0.5M $HClO_4$	0.001149M + 0.001168M	2	279.4	1121	86.38	6

TABLE 2. - Continued. THE VALUE OF THE PARAMETERS G_r AND t_1 ASSOCIATED WITH VARIOUS CHEMICAL REACTIONS UNDER THE CONDITIONS CITED

Reaction investigated	Solvent or diluent	Initial concentration, molarity; or pressure, mm Hg	Reaction order	Temperature, ^oK	G_r, cal/mole	t_1, sec	Ref.
6. Reduction of Pu(IV) by Fe(II) in perchloric acid solution $Pu(IV) + Fe(II) \rightarrow Pu(III) + Fe(III)$	0.5M $HClO_4$	0.001140M + 0.001156M	2	275.7	1099	142.3	6
7. Reaction of sodium cyanide with methyl iodide in aqueous solution $CN^- + CH_3I \rightarrow I^- + CH_3CN$	Water	0.063M + 0.0334M	2	319.3	1288	51.12×10^2	7
	Water	0.063M + 0.0342M	2	304.2	1243	19.74×10^3	7
	Water	0.063M + 0.0254M	2	293.7	1160	82.49×10^3	7
	Water	0.055M + 0.0266M	2	284.6	1137	26.34×10^4	7
8. Reaction of sodium cyanide with tris-(1,10-phenanthroline)-Fe(II) $2CN^- + Fe(Phen)_3(II) \rightarrow Phen + Fe(Phen)_2(CN)_2$	Water	0.105M + 0.0000313M	2	298	1526	72.00×10^2	8
	Water	0.105M + 0.0000313M	2	283	1196	12.58×10^5	8
	Water	0.239M + 0.0000313M	2	298	1679	77.10×10^2	8
	Water	0.239M + 0.0000313M	2	283	1247	96.97×10^4	8
9. Reaction of ferricyanide with 2 mercaptoethanol in aqueous solution $2Fe(CN)_6^{3-} + 2ESH \rightarrow 2Fe(CN)_6^{4-}$	Water	0.0011M + 0.0189M	2	273	962	45.68×10^6	9
	Water	0.0012M + 0.0206M	2	273	992	18.43×10^6	9
10. Reaction of cis-2-butene episulphide with triphenylphosphine $CH_3HCSCHCH_3 + (C_6H_5)_3P \rightarrow CH_3HCCHCH_3 + (C_6H_5)_3PS$	m-xylene	0.314M + 0.314M	2	313	1237	15.52×10^4	10
	N,N-dimethylformamide	0.308M + 0.308M	2	313	1227	11.01×10^4	10
	Cyclohexanone	0.301M + 0.301M	2	313	1249	15.04×10^4	10

TABLE 2. - Concluded. THE VALUE OF THE PARAMETERS G_r AND t_1 ASSOCIATED WITH VARIOUS CHEMICAL REACTIONS UNDER THE CONDITIONS CITED

Reaction investigated	Solvent or diluent	Initial concentration, molarity; or pressure, mm Hg	Reaction order	Temperature, °K	G_r, cal/mole	t_1, sec	Ref.
11. Decomposition of trans-dimeric methyl nitroso $(CH_3NO)_2 \rightarrow 2CH_3NO$	Ethanol	0.0000361M	1	338	1383	56.93×10^4	11
	Ethanol	0.0000361M	1	333	1269	15.44×10^5	11
12. Reaction of bis-p-chlorophenylmercury with mercuric iodide $Hg(ClC_6H_4)_2 + HgI_2 \rightarrow 2(ClC_6H_4)HgI$	Dioxane	0.001M + 0.001M	2	318	1378	26.78×10^2	12
	Dioxane	0.001M + 0.001M	2	308	1362	41.22×10^4	12
13. Reaction of bis-p-fluorophenylmercury with mercuric iodide $Hg(FC_6H_4)_2 + HgI_2 \rightarrow 2(FC_6H_4)HgI$	Dioxane	0.001M + 0.001M	2	318	1292	728	12
	Dioxane	0.001M + 0.001M	2	308	1279	1442	12
14. Reaction of styrene with iodine in carbon tetrachloride $C_6H_5CHCH_2 + I_2 \rightarrow C_6H_5CHI_2CH_2$	CCl_4	0.3472M + 0.000530M		295	320	318	13
	CCl_4	0.3472M + 0.000203M		295	456	133	13
15. Decomposition of hydrogen peroxide vapor with 83.3 mole percent helium $2H_2O_2 \rightarrow 2H_2O + O_2$	Helium	9.60	1	741.7	5296	166.5	14
	Helium	9.60	1	731.6	5019	280.6	14
	Helium	9.60	1	721.6	4899	389.0	14
	Helium	9.60	1	712.8	4588	646.2	14
	Helium	9.60	1	704.7	4488	2165	14

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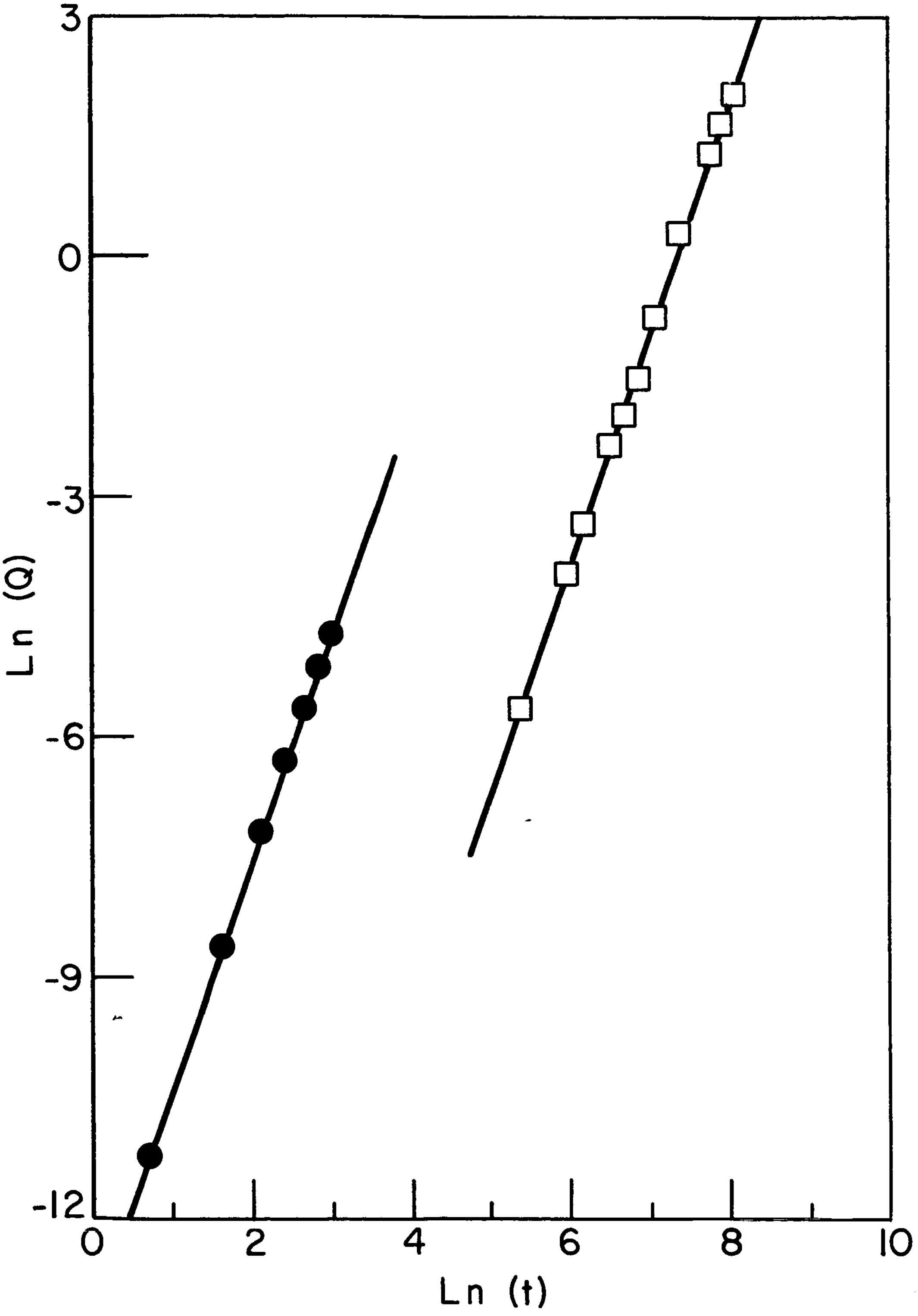

Figure 1. - Decomposition of di-t-butyl peroxide ● (table 2, reaction 1) and dimethyl ether ☐ (table 2, reaction 2).

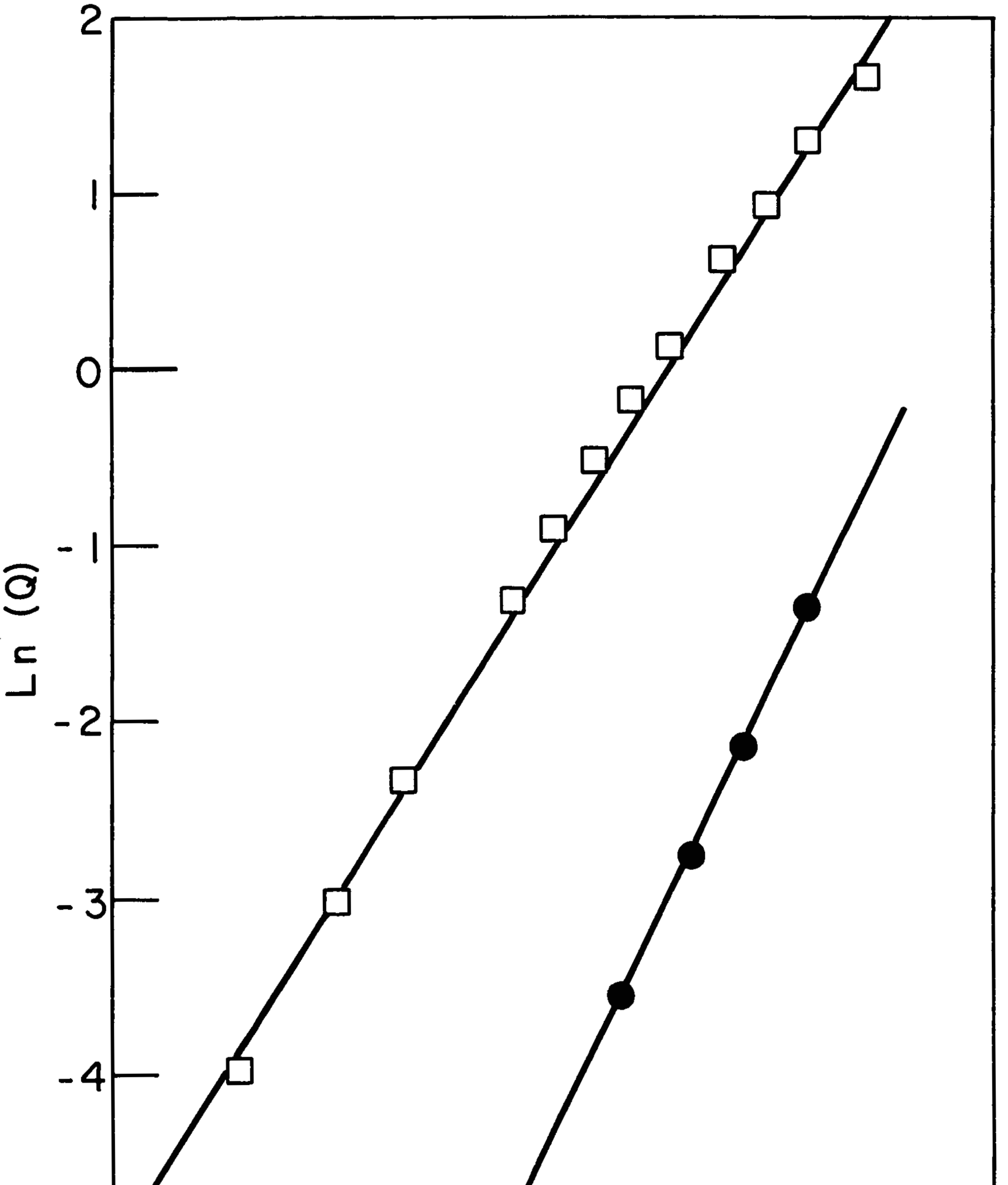

Figure 2. - Decomposition of acetaldehyde □ (table 2, reaction 3) and azo-isopropane ● (table 2, reaction 4).

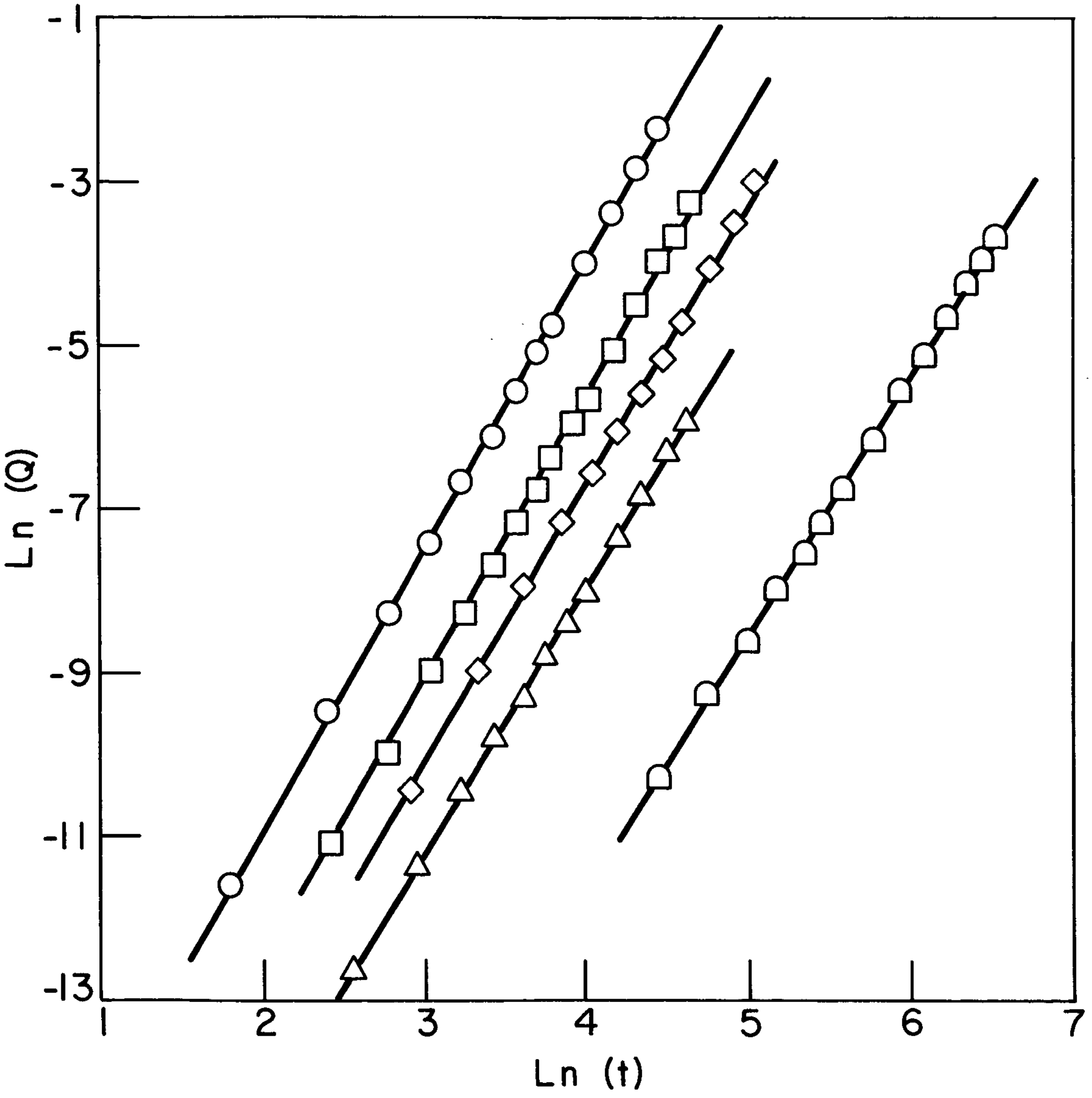

Figure 3. - Decomposition of hydrogen peroxide vapor with 83.3 mole percent helium (table 2, reaction 15). ○ 741.7° K, □ 731.6° K, ◇ 721.6° K, △ 712.8° K, ⌓ 704.7° K.

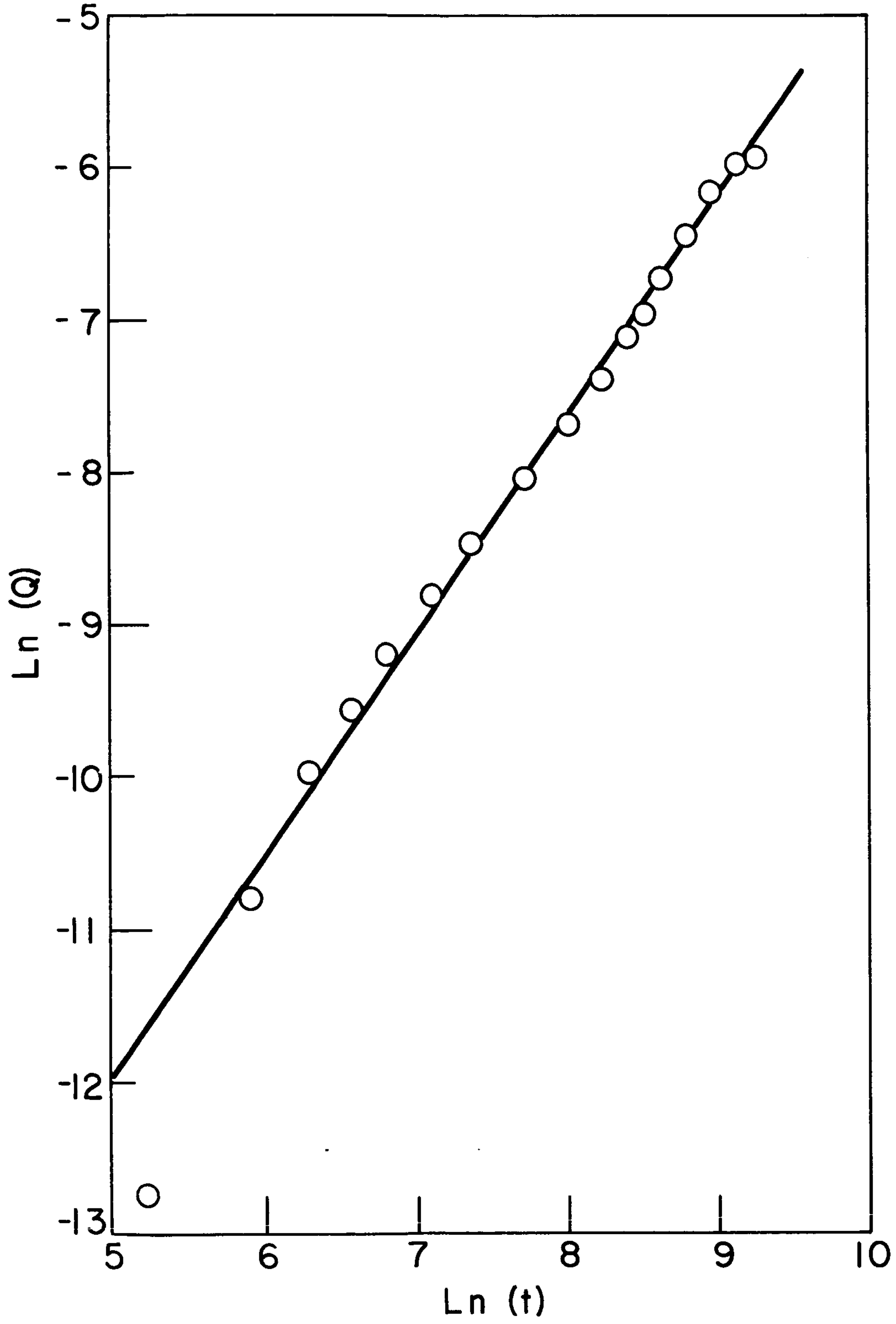

Figure 4. - Decomposition of silver oxide (table 2, reaction 5).

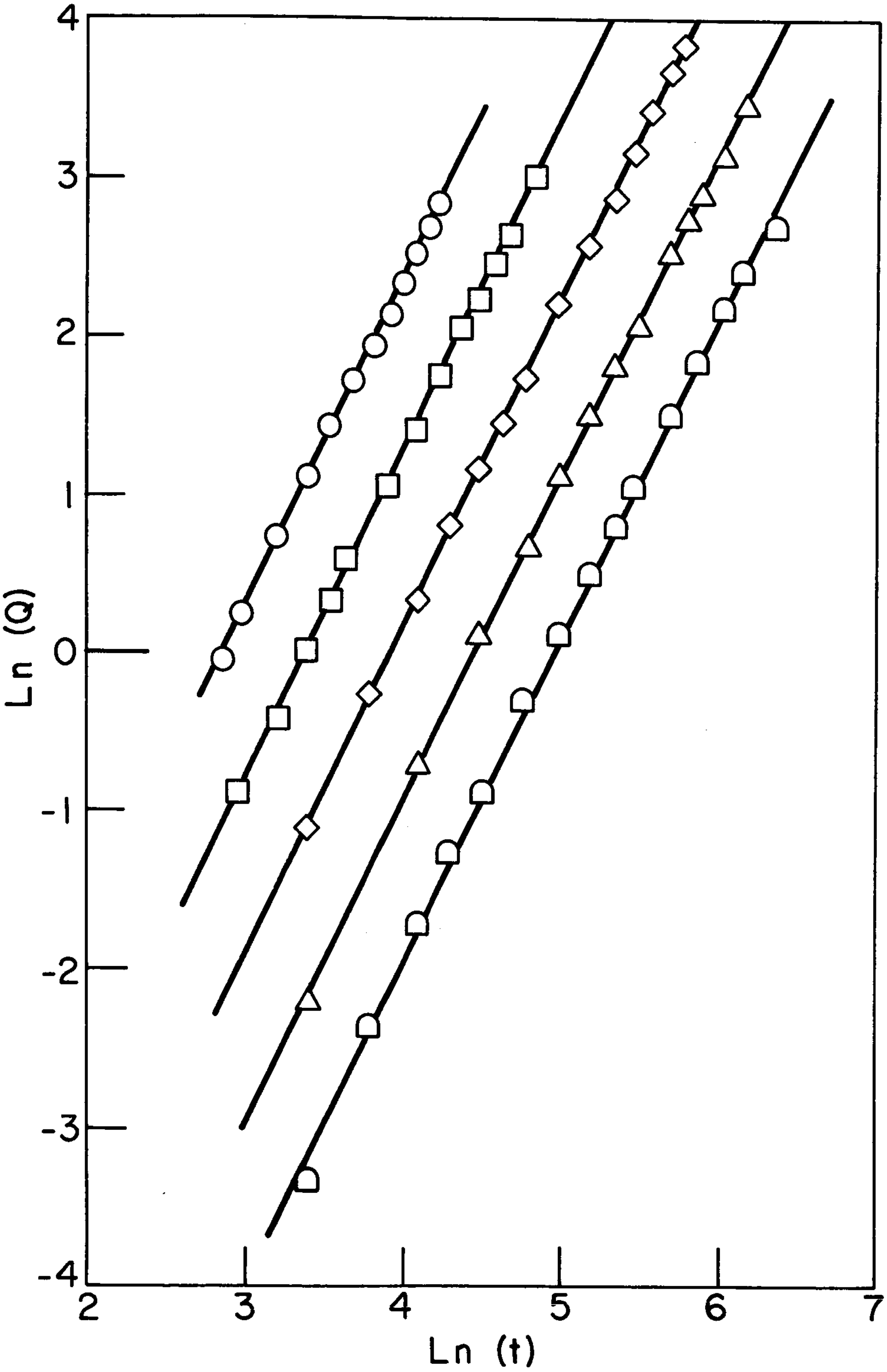

Figure 5. - Reduction of Pu(IV) by Fe(II) in 0.5M perchloric acid solution (table 2, reaction 6). ○ 293.4° K, □ 288.6° K, ◇ 283.4° K, △ 279.4° K, ⌂ 275.7° K.

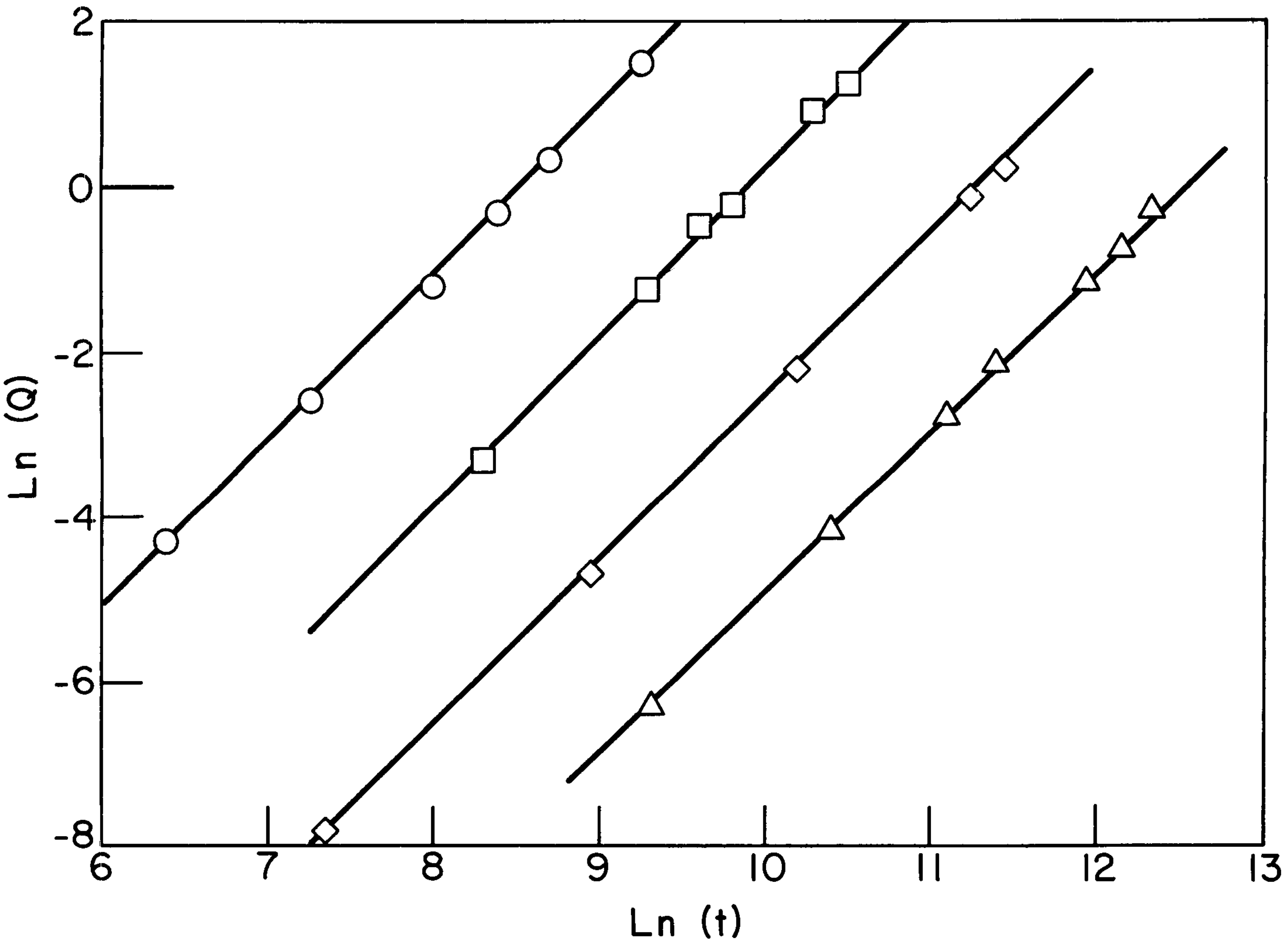

Figure 6. - Reaction of sodium cyanide with methyl iodide in aqueous solution (table 2, reaction 7). ○ 319.3° K, □ 304.2° K, ◇ 293.7° K, △ 284.6° K.

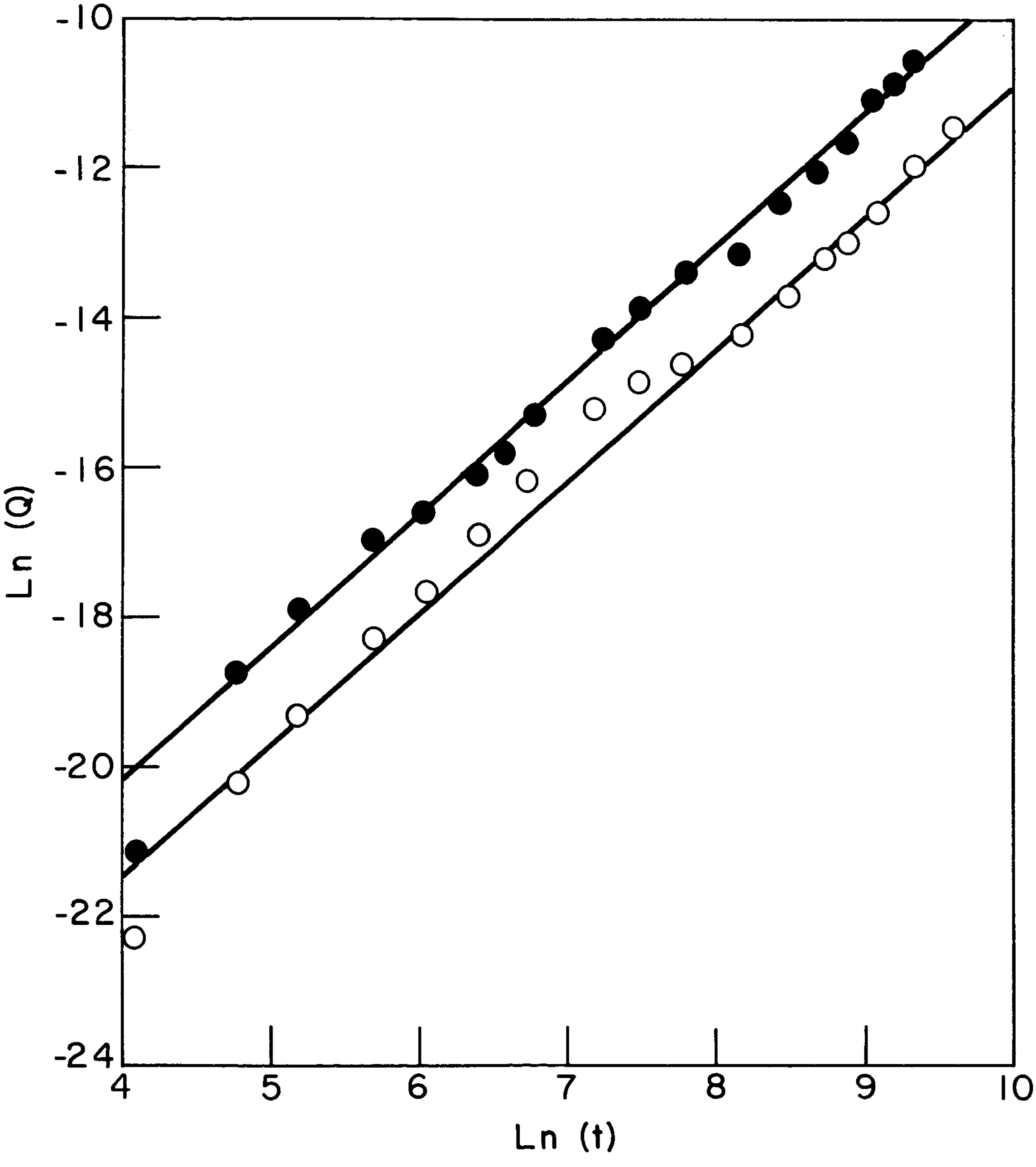

Figure 7. - Reaction between potassium ferricyanide and 2-mercapto-ethanol in aqueous solution (table 2, reaction 9). Initial concentrations - ○ ferricyanide 0.00110M, 2-mercapto-ethanol 0.0189M; ● ferricyanide 0.00119M, 2-mercapto-ethanol 0.0206M.

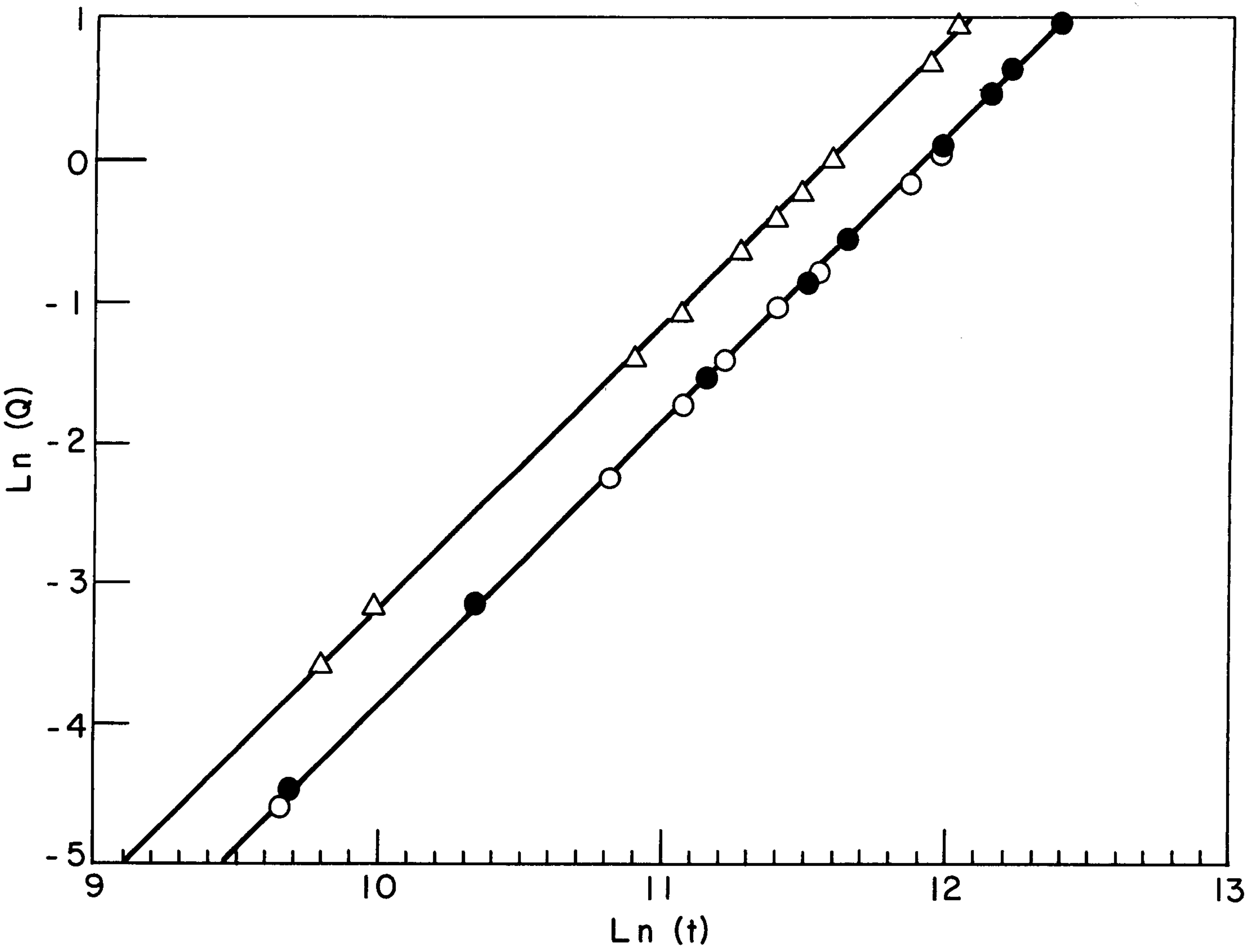

Figure 8. - Reaction of cis-2-butene episulphide with triphenylphosphine in △ N,N-dimethylformamide, ○ m-xylene, and ● cyclohexanone (table 2, reaction 10).

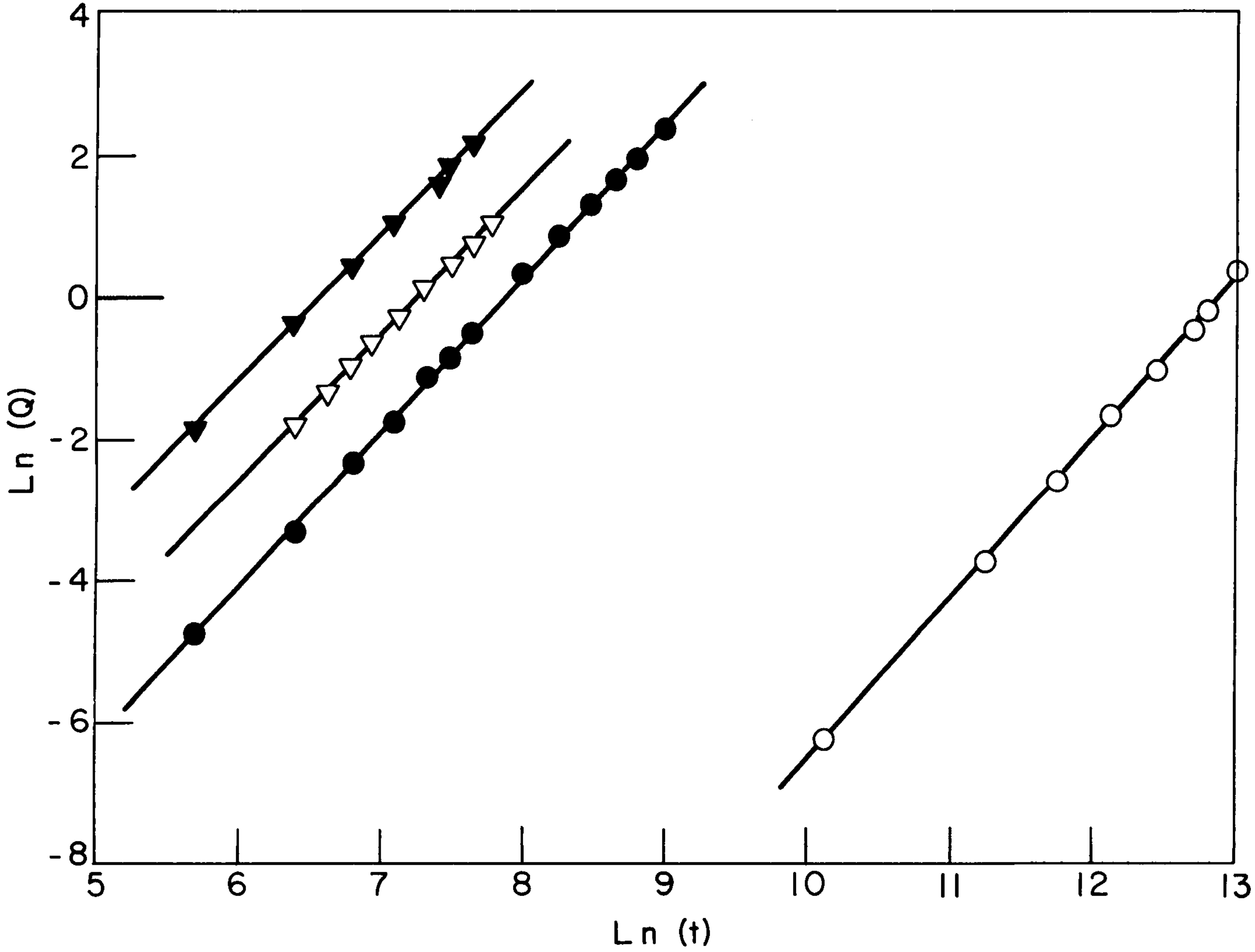

Figure 9. - Reaction of bis-p-chlorophenylmercury (table 2, reaction 12). ● 308° K, ○ 318° K; and bis-p-fluorophenylmercury (table 2, reaction 13). ▼ 308° K, ▽ 318° K, with mercuric iodide in dioxane.

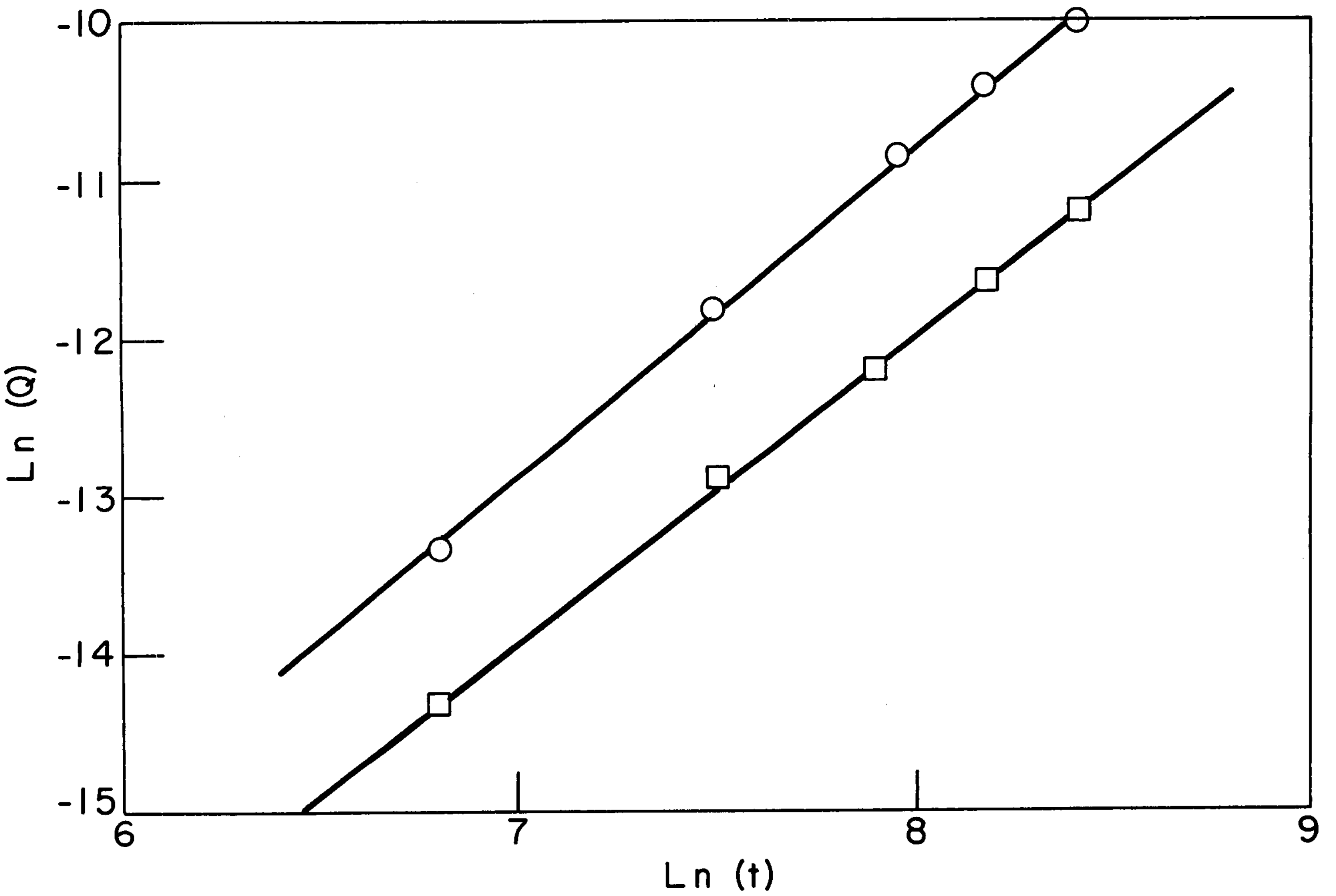

Figure 10. - Decomposition of trans-dimeric methyl nitroso in ethanol (table 2, reaction 11).
○ 338° K, □ 333° K.

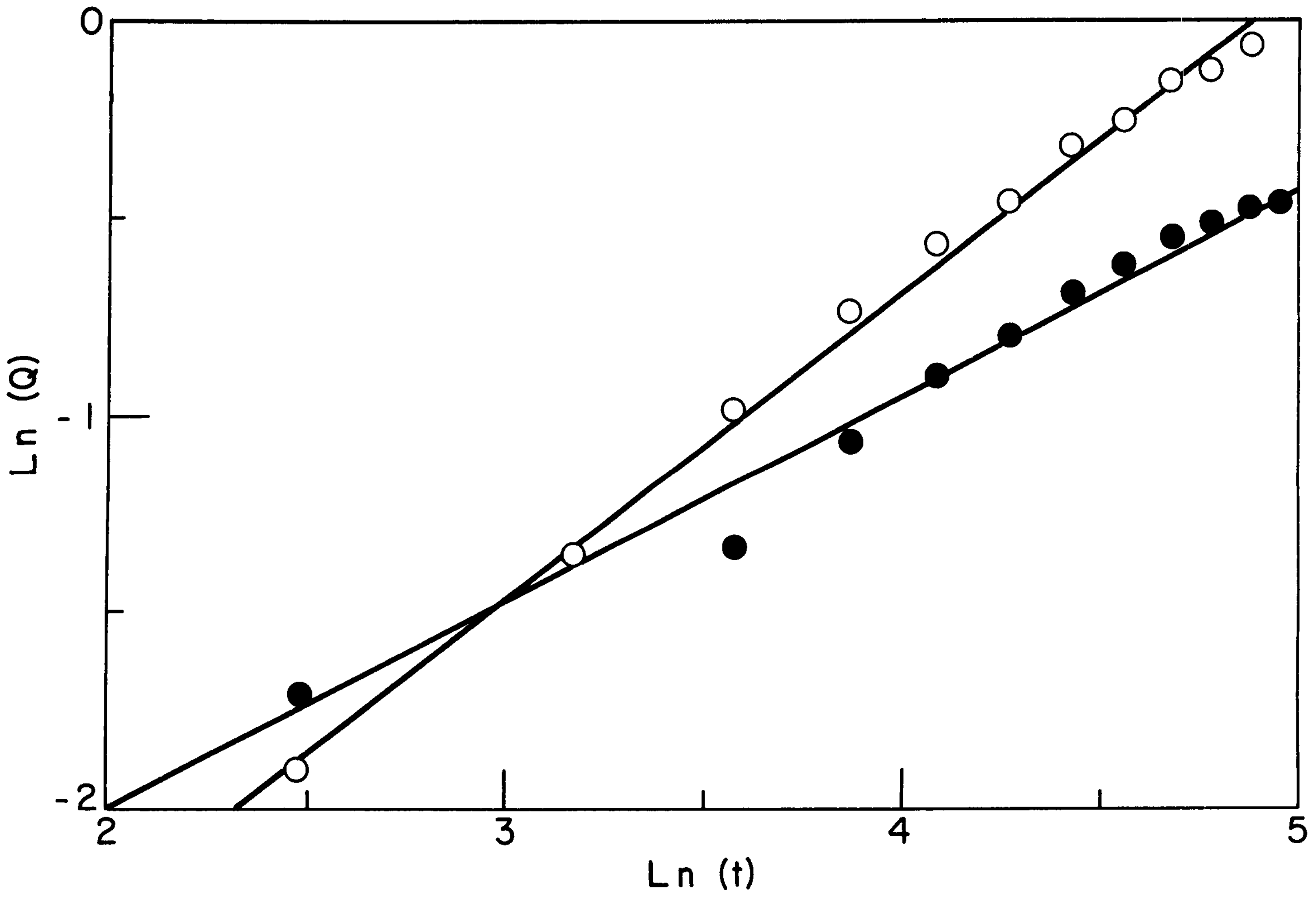

Figure 11. - Reaction of styrene and iodine in carbon tetrachloride (table 2, reaction 14). Initial concentration - ● styrene 0.3472M, iodine 0.00053M; ○ styrene 0.3472M, iodine 0.000203M.